SOLVOLEACHING OF (LANDFILLED) INDUSTRIAL RESIDUES AND A LOW-GRADE LATERITE ORE WITH DILUTED HCl IN THE IONIC LIQUID ALIQUAT 336

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Introduction

The EU and the rest of the world are experiencing an ever-smaller metal supply and an ever-increasing amount of industrial waste. On the one hand, economically relevant metals such as nickel, chromium, antimony, lead or zinc are needed for everyday life and modern technologies. Despite their importance, many governments are facing problems to ensure their supply. On the other hand, environmentally-harmful sludges from steel, alumina or zinc refining are produced in the order of millions of tonnes per year. These sludges are frequently disposed in landfills, and could pose an environmental hazard if rainwater infiltrates the waste and percolates the surroundings. Accordingly, the landfilling costs, dependent on the local taxes and the sludge composition, are increasingly growing.

The objective of this study is to analyse the efficient recovery of economically relevant metals from low-grade nickel laterite ores and (landfilled) industrial processes residues, using “solvoleaching”. Attention is also paid to maximising the extraction yield of hazardous elements so that the remaining solid that was not dissolved (consumed) during the solvoleaching process, can be reused as construction material or agricultural amendment.

Solvoleaching consists of applying organic liquids (complexing agents, solvents, acidic extractants, organic acids *etc.*) for extracting metals from a solid, with the aim to reduce the volume of the aqueous phase (< 50%), compared to conventional leaching.[1] In addition, it can result in higher selectivity for (a) targeted metal(s) than conventional hydrometallurgical leaching. Here, a system based on solvoleaching is applied to a low-grade nickel laterite ore and three industrial residues. Specifically, the four different materials examined were: (1) a low-grade nickel laterite ore from Poland (LAT), (2) a chromium-rich sludge from the stainless steel industry (CRS), (3) jarosite residue from zinc production (JAR) and (4) a zinc-rich sludge from the metal industry (ZRS). These materials are significant because there are large deposits of nickel laterite ores in Poland that can be exploited as an open pit mine for the recovery of this relatively expensive metal (12,230 $/t, London Metal Exchange, 9

November 2017), and, concurrently, there are millions of tonnes of sludge being disposed every year.

Materials and methods

The four materials investigated have different characteristics. LAT is composed of Mg-Fe-Ni silicates, hydroxides and oxides, while JAR contains Na-K Fe sulphate hydroxides, Pb and Zn sulphides, and Na-Ca aluminium silicate hydrates. CRS and ZRS are mainly constituted by Ca sulphate hydrate (mostly gypsum). In the former, CaF_2, Cr-Ni oxides and Ni-Cr-Mg iron oxides are present, while in ZRS, $CaCO_3$, Ca-Zn hydroxide hydrates, Zn oxide and Fe sulphate hydroxide hydrates are present. Depending on the material, there is a different major element that predominates: silicon in LAT (23 wt%), elemental sulphur in JAR (30 wt%) and calcium in CRS and ZRS (25 wt%). All materials contain much higher concentrations of iron (10-15 wt%) in comparison to those of the economically relevant metals (1-4 wt%). Depending on the material, these are: 1.1 wt% Ni and 0.5 wt% Cr in LAT; 2.2 wt% Cr and 1.6 wt% Ni in CRS; 3.2 wt% Pb, 2.5 wt% Zn and $8.7 \cdot 10^{-2}$ wt% Sb in JAR; and 4.1 wt% Zn in ZRS. Iron is an unwanted element for the downstream processes and when dissolved in the leachate, it needs to be removed before the recovery of the desired metals, because iron would compete with them, decreasing the extraction yields of the elements of interest.

The materials were dried for 48 h at 105°C and sieved to 400 µm size on a vibratory shaker Analysette 3 from Fritsch. No pre-treatment other than comminution or manual disaggregation and sieving was applied, in order to avoid highly costing processes. The remaining moisture content was verified with a HC103 Mettler-Toledo moisture analyser, (1/50 mg/s, 150°C drying temperature). The particle size distributions were analysed by laser diffraction with a Malvern 3000 laser diffractometer, using water as the dispersant medium and 1.555 as the refractive index of the solid samples. The external specific surface area was calculated *via* the Brunauer–Emmett–Teller (BET) equation, determined with a Quantchrome NOVA 2200e analyser, after degasification of the samples under vacuum at 100°C for 25 h. The content of nitrogen, carbon and hydrogen was measured in a Thermo Scientific FLASH 2000 Elemental Analyser. The lixiviant used was Aliquat® 336 (a mixture of quaternary ammonium chlorides) containing ≤ 20 wt% water and different amounts of HCl (from 0.03 to 2.5 M HCl). The content of HCl in Aliquat was calculated measuring the HCl concentration of aqueous solutions with a refractometer (Anton Paar Abbemat Series) and extrapolating the results in a polynomial equation (Adj. R^2 = 0.99998).

The solvoleaching experiments were performed by mixing the dried materials with the lixiviant, at a liquid/solid ratio of 10 mL/g, using thermoshakers at 60°C, for 4 h, at 2,000 rpm. The metal content in the leachate was analysed *via* Total Reflection X-ray Fluorescence (TXRF) with a Bruker S2 PICOFOX™.

Results and discussion

All the dried and sieved materials had a very fine grain size: 90 vol% was < 107-120 µm for LAT, CRS and ZRS, and was < 302 µm for JAR (Figure 1). The external specific surface areas varied depending on the origin of the materials: lower values were for the materials coming from a hydrometallurgical iron precipitation process (9, 62 and 63 m^2/g in JAR, CRS and ZRS, respectively), while higher values were for the natural laterite ore (166 m^2/g). The CHN analysis showed that no nitrate or ammonium phases were present in the materials and carbon was only present in ZRS (4 wt%), in the form of calcite.

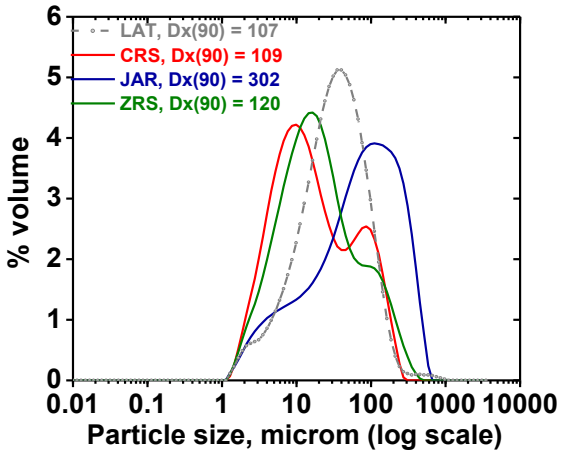

Figure 1: Volume percentage of particles within the respective size, for nickel laterite (LAT), Cr-rich sludge (CRS), jarosite (JAR) and Zn-rich sludge (ZRS) materials

There are three major groups of solvolixiviants: (1) mineral acids in water-miscible organic solvents, (2) organic acids (alone or in water) and (3) extractants (alone or in water-immiscible organic diluents). A screening test for rapid comparing, assessing and scoring of different solvolixiviants was performed, taken at least one example of each solvent group. Based on the leaching yields, the selectivity and the price, the quaternary ammonium chloride ionic liquid Aliquat 336 was selected for the next tests where the effect of the HCl concentration in Aliquat 336 on the leaching was studied. In all cases, Aliquat 336 (apolar) was saturated with water and then, forcedly mixed with different HCl solutions (polar) to prepare the different dilutions of HCl in Aliquat 336. The remaining HCl aqueous solution not uptaken by Aliquat 336, was discarded and the homogeneous organic solutions of HCl/Aliquat 336 were used as lixiviants. A strong effervescence reaction was observed when adding the lixiviant to

the ZRS, probably due to the exothermic reaction of HCl with calcite, which forms CO_2 gas, matching with the gas scape noticed when opening the vials at the end of the tests. After leaching, the formation of a small volume of aqueous solution (immiscible with the HCl/Aliquat 336 leachate), was observed. The volume of the aqueous solutions was larger when Aliquat 336 had higher content of HCl and when leaching LAT and JAR than when leaching CRS and ZRS. The water may come from the lixiviant itself, from the reaction of HCl with oxides and hydroxides, and from redox reactions, *e.g.*, oxidation of sulphides.

In the case of JAR and ZRS, the main metals remained in the organic leachate (HCl/Aliquat 336). Only antimony from JAR was concentrated in the aqueous leachate. The leaching efficiencies of Pb, Zn and Fe increased with the amount of HCl in Aliquat 336, but the process is more selective towards the desired metals at the lowest HCl content (Figure 2 and Figure 3). The leaching behaviour of As, Pb and Fe from JAR was identical, what indicates their association in the same mineral phases, *i.e.*, in galena. The selective leaching of Zn against Fe in ZRS remained at higher amounts of HCl in Aliquat 336 than in the case of JAR. This is beneficial because it provides higher leaching efficiencies of Zn without dissolving more iron. However, at above 1.5 M HCl in Aliquat 336, Fe and Zn were totally dissolved in ZRS. This may be caused by the high dissolution of calcite by HCl, which would increase the temperature and, therefore, the solubility in diluted HCl of sulphates (the main solid phase in the sludge).

In the case of LAT and CRS, the main metals (Ni and Cr) went to the newly formed aqueous leachate and the iron remained in the organic leachate. This provides an advantageous situation to concentrate and separate the economically relevant metals from iron. In this case, the leaching efficiencies cannot be calculated because of the inability to accurately determine the volume of the newly created aqueous leachate. However, rough estimations gave values > 90% of Ni leached from LAT and > 90% of Ni and > 90% of Cr from CRS, with almost no iron.

The mechanism underlying this kind of solvoleaching process could be thought as a double process. One would be the dissolution of mineral phases such as hydroxides and sulphides in JAR, or oxides and sulphates (namely gypsum) in CRS, by HCl. The other mechanism would be the formation of soluble anionic chloro complexes $[MeCl_4]^{2-}$, that would go to the Aliquat 336 leachate *via* anion exchange $(A336)_2MeCl_4$ (with Me = Ni, Zn, Fe, Pb) and soluble cationic aquo complexes that would go to the aqueous leachate ($[Ni(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{3+}$). Depending on the affinities and the stability constants of the metal-complexes formed, the metals will distribute differently between the aqueous and the HCl/Aliquat 336, leachates.

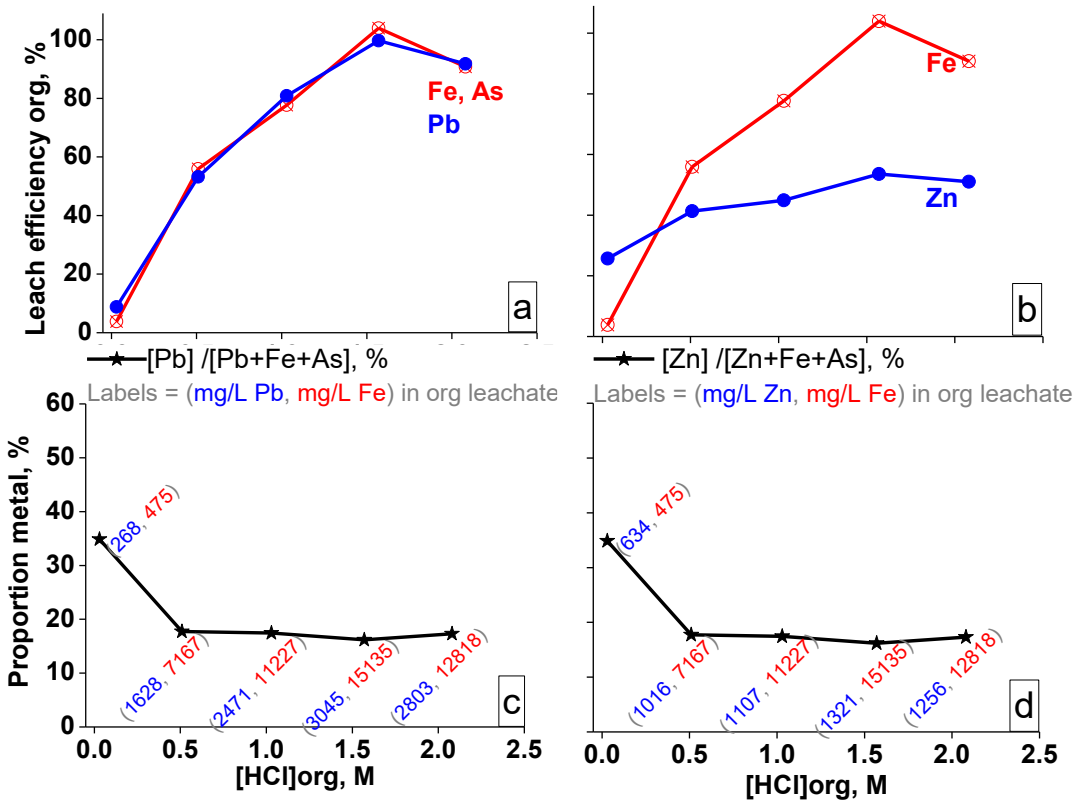

Figure 2: Leaching efficiencies of Fe, As, Pb, Zn (a, b) and content of Fe, Zn and Pb in the leachate (c, d: labels = concentration (mg/L) in the leachate, curve = proportion related to Fe) in the JAR at different HCl concentrations in Aliquat 336 ([HCl]org)

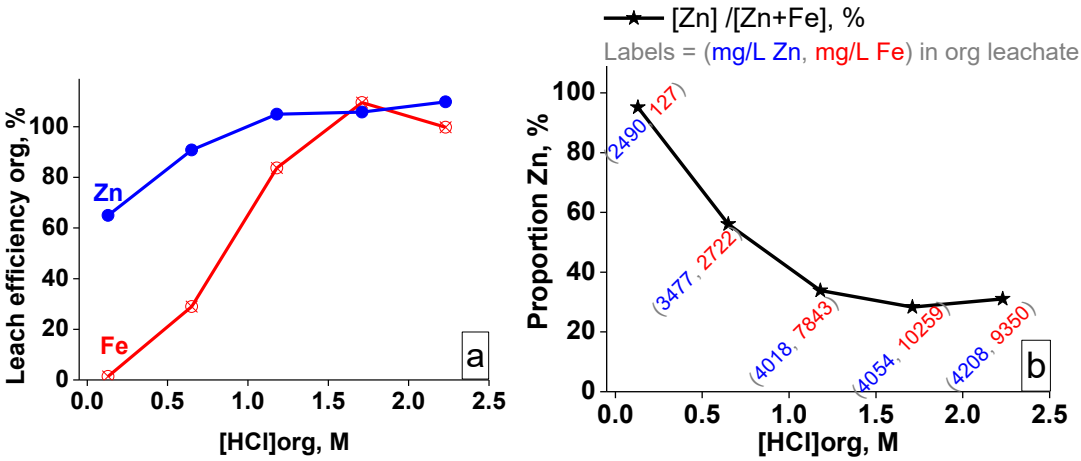

Figure 3: Leaching efficiencies of Fe and Zn (a) and content of Fe and Zn in the leachate (b: labels = concentration (mg/L) in the leachate, curve = proportion related to Fe) in the ZRS at different HCl concentrations in Aliquat 336 ([HCl]org)

Conclusions

This work focussed on the recovery *via* solvometallurgical leaching of valuable metals like Zn, Pb, Ni and Cr from LAT, JAR, CRS and ZRS. The selective dissolution against the main impurities (Fe) was also assessed. The content of HCl in the ionic liquid Aliquat 336 had a major influence on the leaching efficiencies and the selectivity: the lower the acid content in Aliquat 336, the higher the selective leaching, and the lower the leaching efficiency. Only in the case of Pb from JAR, there was no change in its leaching selectivity against Fe: the leaching of Fe, As and Pb from JAR was coupled together and had the same tendencies, suggesting that the major Pb mineral phase (galena) has also Fe and As entrapped. Although leaching tests were performed with one organic lixiviant, two immiscible leachates were normally produced: the corresponding organic one (a large part of the total volume) and an aqueous leachate (a small part of the total volume). This is important for the separation of the metals, because the different metal complexes formed showed different affinities towards one or another leachate. Thus, Ni and Cr were concentrated in the aqueous leachate, while Pb, Zn and Fe in were concentrated in the organic leachate.

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